Quarterly Progress Report on

Standard Agreement No. 04-329

For the Period

May 1, 2007 through August 31, 2007

Development of an Improved VOC Analysis Method for Architectural Coatings

Prepared for California Air Resources Board
and the California Environmental Protection Agency

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Disclaimer-

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Acknowledgements

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I. Work This Reporting Period

This report summarizes work performed on the project from May 1, 2007 through August 31, 2007.

A. Task 2 Activities

During this time period, work was continued on Task 2 activities including

- Requesting, cataloging and splitting of samples
- Refinement of testing procedures
- Preliminary analysis of samples

B. Samples

Samples of the 86 coatings chosen by CARB for analysis for this project were ordered directly form the manufacturer. We have obtained 73 coatings. Most of these were obtained directly from manufacturers. A few were purchased from retail outlets. In some cases, substitute coatings were chosen when we were unable to obtain a particular product. We have obtained coatings representing all but two of the coatings categories defined by CARB earlier in the project. Eleven of these coatings are two component systems. Thus a total of 84 samples have been obtained. We could not obtain samples of multi-color coatings nor of solvent-based traffic coatings. Water-based traffic coatings have essentially replaced solvent-based traffic coatings according to Cal Trans. It is possible a few samples may be added to this list but we feel these coatings accurately represent the coatings sold in California. The list of coatings currently included in this study is given in Table 1.

After thorough mixing, each one gallon sample was divided into four one quart samples to be used for testing by us and possibly by other laboratories as part of the validation study associated with this project. In a few cases, either 5 gallon or 1 quart samples were obtained. Initially, the density of each coating is determined using a weight per gallon cup. For two component coatings, the density of each component is determined separately. For single component coatings, the solids fraction is then determined using ASTM 2369. Great care is taken to insure consistent amounts of coating and water (or other suitable solvent) are used in the solids determination since we have determined in previous work that the amount of coating and water (or other solvent) can affect the results obtained, especially if high boiling materials are present. For two component coatings, the components are mixed in the appropriate ratio and a sample of the coating is analyzed using a procedure similar ASTM 2369 with no added solvent. Details were explained in our April, 2007 progress report. Results of densities and fraction solids for those coatings analyzed so far are given in Table 2.

Table 1. Coatings undergoing VOC analysis

					WATERBORNE					SOLVENTBORNE		
in	run	split		Coating Category	Low VOC	High VOC	High Multi	Low Solids	High Multi	Low Solids	High Solids	High Exempt
y	y	y	1	Fire Resistive	X							
y	y		2	Recycled	X							
y	y	y	3	Industrial Maintenance					X-2K			
y		y	4	Bituminous Roof	X							
y		y	5	Bituminous Roof		X						
y		y	6	Driveway Sealer	X							
y		y	7	Metallic Pigmented	X							
y	y	y	8	Faux Finishing		X						
y	y	y	9	Stains - Clear/Semitransparent				X				
y	y	y	10	Stains - Opaque	X							
			13	Varnishes - Clear		X	X					
y			14	High Temperature								X
y	y	y	14-1	Industrial Maintenance							X-2K	
y	y	y	14-2	Industrial Maintenance							X-2K	
y	y	y	14-3	Industrial Maintenance							X-2K	
y	y	y	15-1	Industrial Maintenance							X-2K	
y	y	y	15-2	Industrial Maintenance							X-2K	
	y	y	15-3	Industrial Maintenance							X-2K	
y	y	y	24	High Temperature								X
y	y	y	25	Swimming Pool					X-2K			
y	y	y	26	Swimming Pool			X-2K					
y			29	Varnishes-clear		X						
y	y	y	32-1	Lacquers	X							
y	y	y	32-2	Primer/stainblock	X							
y	y	y	34	Dry Fog	X							
y	y	y	35	Dry Fog	X							
y			36	Faux Finishing	X							
y	y	y	37	Roof	X							
y	y	y	38	Waterproofing Concrete/Masonry Sealers	X							
y	y	y	39	Bituminous Roof	X							
y	y	y	40	Driveway Sealer	X							
y	y	y	41	Driveway Sealer	X							
y	y	y	43	Roof	X							
y			44	Magnesite Cement								X
y			44-2	Magnesite Cement								X
y	y	y	45	Varnishes - Clear			X-2K					
y			48	Wood Preservatives				X				
y	y	y	50	Mastic Texture	X							
y	y	y	51	Waterproofing Concrete/Masonry Sealers	X							

Table 1. Coatings undergoing VOC analysis (con’t.)

					WATERBORNE				SOLVENTBORNE			
in	run	split		Coating Category	Low VOC	High VOC	High Multi	Low Solids	High Multi	Low Solids	High Solids	High Exempt
y			52	Bond Breakers				X				
y			53	Form Release Compounds							X	
y	y	y	55	Rust Preventative		X						
y		y	56	Low Solids	X			X				
y	y	y	57-1	Lacquers						X		X
y	y	y	57-2	Lacquers						X		X
y	y	y	57-3	Lacquers						X		X
y			59	Floor		X-2K						
y			60	Metallic Pigmented		X						
y			61	Varnishes - Clear		X						
y			62	Stains - Clear/Semitransparent								X
y	y	y	63	Floor		X						
y	y	y	64	Waterproofing Sealers				X				
y	y	y	65	Waterproofing Sealers	X			X				
y			73	Traffic Marking	X							
y	y	y	75	Bituminous Roof	X							
y	y	y	76-1	Faux Finishing		X		X				
y		y	76-2	Faux Finishing		X		X				
y	y	y	76-3	Faux Finishing		X		X				
y		y	76-4	Faux Finishing		X		X				
y	y	y	76-5	Faux Finishing		X		X				
y	y	y	76-6	Faux Finishing		X		X				
y			77	Lacquer								X
y	y	y	79	Sanding Sealers				X				
y	y	y	80	Stains - Opaque	X			X				
y	y		81-1	Concrete Curing Compounds	X			X				
y	y		81-2	Concrete Curing Compounds	X			X				
y			82-1	Waterproofing Concrete/Masonry Sealers	X			X				
y			82-2	Waterproofing Concrete/Masonry Sealers	X			X				
y	y	y	83	Quick Dry Primer, Sealer, and Undercoater	X							
y	y	y	84	Shellacs - Clear						X		
y	y	y	85	Shellacs - Clear						X		
y	y	y	86	Wood Preservatives	X			X				
y	y	y	87	Varnish						X		

1. "Low VOC": <=3% VOCs by weight. "High VOC": >=10% VOCs by weight. "High Exempt": >=10% Exempt Compounds by weight.
2. "High Multi": Categories that have more than 10% multi-component products, by sales volume.
3. "Low Solids": 0-20% solids by volume. "High Solids": 80-100% solids by volume.
4. "Low Solids" and "High Solids" products only include single-component coatings.
   The other classifications include both single-component and multi-component coatings.

Table 2 Fraction solids and densities of coatings samples
Two component coatings have densities for both a and b components; fraction solids is for mixed coating

Sample	fraction solids	density (lbs/gal)	density (g/L)
1	0.478	8.743	1047
2	0.501	10.940	1311
3a	0.880	11.725	1405
3b		12.720	1524
4	0.526	8.637	1035
5	0.465	7.029	842
6	0.562	11.451	1372
7	0.363	9.145	1096
8	0.214	8.876	1063
9	0.177	8.498	1018
10	0.439	9.506	1139
14-1a	0.970	14.341	1718
14-1b		8.081	968
14-2a	0.856	14.481	1735
14-2b		11.905	1426
14-3a	0.883	9.666	1158
14-3b		16.146	1934
15-1a	0.974	9.632	1154
15-1b		11.834	1418
15-2a	0.961	9.587	1148
15-2b		13.535	1622
15-3a	0.847	10.983	1316
15-3b		13.251	1587
24	0.567	9.435	1130
25a	0.815	15.004	1798
25b		7.416	888
26a	0.568	8.563	1026
26b		14.933	1789
32-1	0.504	11.339	1358
32-2	0.566	10.714	1284
34	0.516	10.410	1247
35	0.543	11.207	1343
37	0.653	11.308	1355
38	0.578	10.927	1309
39	0.474	8.440	1011
40	0.574	11.418	1368
41	0.499	10.317	1236
43	0.475	10.329	1237
45a	0.282	8.321	997
45b		6.766	811
50	0.643	11.634	1394
51	0.219	8.430	1010
55	0.433	10.328	1237
56	0.064	8.231	986
57-1	0.261	7.571	907
57-2	0.218	7.380	884
57-3	0.252	7.493	898
63	0.412	9.471	1135
64	0.200	8.584	1028
65	0.098	8.426	1009
75	0.532	7.319	877
76-1	0.152	8.966	1074
76-3	0.134	8.832	1058
76-6	0.149	8.926	1069
79	0.221	8.514	1020
80	0.068	8.553	1025
81-1	0.189	8.303	995
81-2	0.349	8.138	975
82-1	0.113	8.444	1012
82-2	0.293	8.624	1033
83	0.505	10.534	1262
84	0.228	7.283	872
85	0.224	7.308	875
86	0.039	8.373	1003
87	0.245	6.954	833

C. Refinement of Testing Procedures

During this reporting period we have continued to concentrate on development of analysis methods. We have made minor modifications to ASTM 6886 for analysis of waterborne air-dry coatings, developed a comprehensive method for analysis of two-component (2K) coatings, and developed a method for direct analysis of hazardous air pollutants (HAPs) in coatings. We now believe we have methods available for use in determination of VOCs for virtually all the coatings in the CARB architectural coatings survey. A very limited number of coatings present challenges requiring additional analysis methods, in particular headspace analysis gas chromatography. We discuss each of these methods below and give details of the proposed methods at the end of this report. The detailed procedures are written in the style of ASTM methods since we plan to submit these methods to ASTM for consideration as new or modified VOC analysis methods.

We have tested these procedures on most of the coatings received to date. Examples of results for some of the more interesting samples are given below. Detailed analyses of all coatings tested will be provided in our next progress report.

Analysis of One-component Coatings

In our last report, we outlined a proposed modification of ASTM D-6886 using isopropanol (2-propanol) as the dilution solvent instead of tetrahydrofuran (THF) and using ethylene glycol diethyl ether (EGDE) as the internal standard. Isopropanol is less toxic than THF and does not co-elute with any of the major VOCs found in water-based coatings. This modification is suitable for use with all waterborne air-dry coatings having material VOC content between zero and five percent but has been used successfully with higher VOC content waterborne coatings. The method may also be used to measure the exempt VOC content (acetone, methyl acetate, t-butyl acetate and p-benzotrifluoride) of waterborne and solventborne coatings. Since some VOCs elute with the same rentention times on the 5 % phenyl/95 % methylsiloxane (PMPS) column normally used for these analyses, an additional analysis using a wax column may be required. A sample analysis is given below.

Analysis of Two-component (2K) Coatings

Two-component coatings present particular challenges for VOC determination. In principal, the method should duplicate, as closely as possible, the actual procedure use in the field to mix and apply the coating. We presented an overall method for analysis of these coatings in our last report. In this new method the multi-component mixture is allowed to cure in a sealed headspace vial in which the VOC emissions are retained. Addition of acetone containing an internal standard transfers the emissions into the solvent and gives a solution which can be analyzed by direct injection into a gas chromatograph. Since the method provides a direct determination of the individual VOCs it is also suitable for quantitative determination of amounts of any hazardous air pollutants (HAPs) in these coatings. We have refined the procedures given in our last report and provided details so other laboratories can duplicate our analyses on 2K coatings.

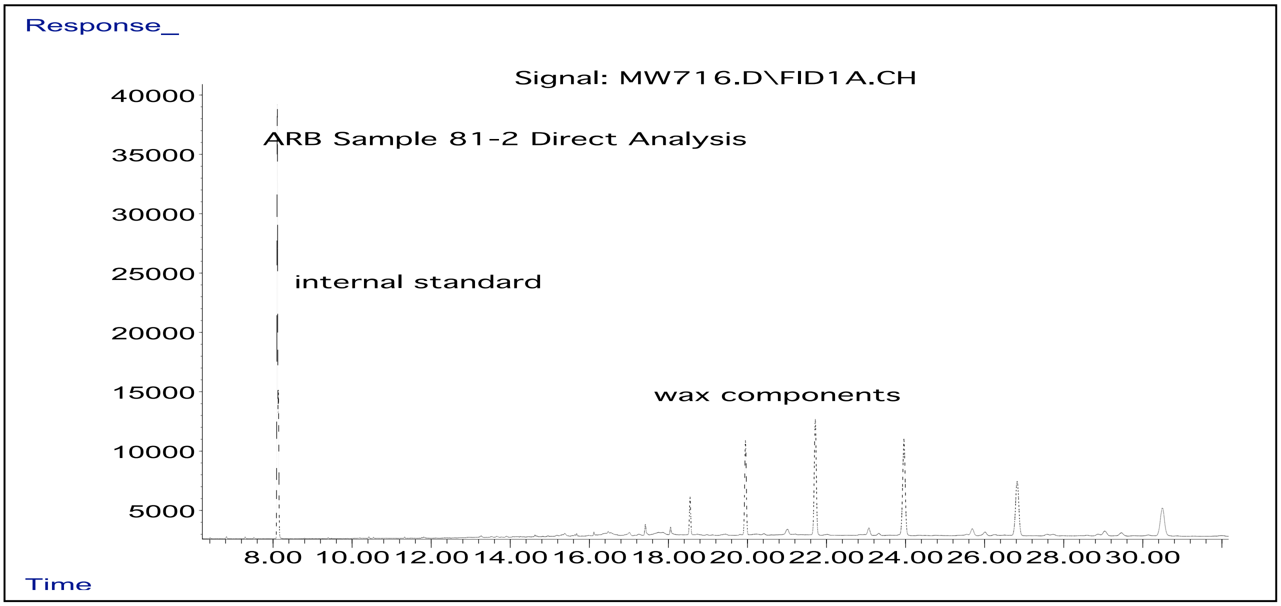
Analysis of Hazardous Air Pollutants in Solventborne Air Dry Coatings

In conjunction with our development of the other test methods, we have developed a method specifically for analysis of hazardous air pollutants (HAPS) in solvenborne air dry coatings. In summary, a known weight of coating is dispersed in tetrahydrofuran (THF) or acetone, internally standardized, and analyzed by capillary gas chromatography to give a speciated composition of the VOCs in the coating. The HAPs present in the coating are identified and measured relative to the internal standard. GC/FID or GC/MS using solid phase microextraction (SPME) of the coating may be used to facilitate identification of the volatile compounds present in a coating.

Sample Analyses

Sample 81-2: Sample 81-2 is a low solids, waterborne, low VOC concrete curing compound. This sample was analyzed by direct injection using the modification of ASTM D6886. The chromatogram is shown below in Figure 1.

Figure 1 Sample 81-2 Chromatogram



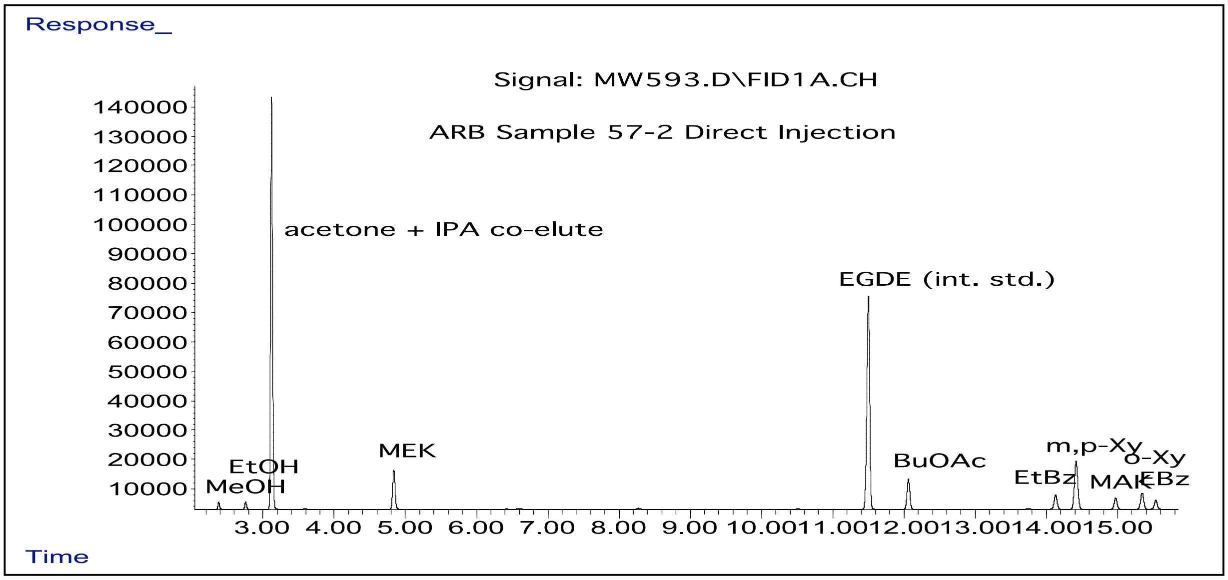
No peaks are present (other than solvent and internal standard) for retention times less than 16 minutes (Texanol, for example, has a retention time of 13.5 minutes). The peaks beyond 16 minutes are due to hydrocarbons, typically found in waxes. Even though this is a "zero VOC" coating, we can still determine the amounts of semi-volatile components present. This sample again shows the value of defining a retention time marker for definition of VOC. The analysis of this coating is shown below:

Analysis of Sample 81-2

Cpd	fraction
EGDE	0.0000
HC	0.0009
HC	0.0029
HC	0.0045
HC	0.0047
HC	0.0034
HC	0.0023
HC	0.0013
Total	0.0199

Sample 57.2: Sample 57.2 is a low solids, high exempt solventborne lacquer. Upon analysis by gas chromatography using a 30 m by 0.25 mm 5 % phenyl/95 % methyl siloxane column, the chromatogram shown below in Figure 2 is obtained.

Figure 2 Sample 57.2 Chromatogram



The large peak at a retention time of 3 minutes is primarily due to acetone. However, under these conditions, 2-propanol (isopropyl alcohol) co-elutes with acetone. In order to determine the amount of acetone (an exempt solvent) accurately, the peaks must be separated. This can sometimes be accomplished by changing the temperature program on the gas chromatograph. An alternate, and often more successful, method is to use a secondary column for analysis, in this case a more polar wax column. The analysis of Sample 57.2 is shown below. The fractions for acetone and methyl acetate are not included in the overall total since they are exempt compounds.

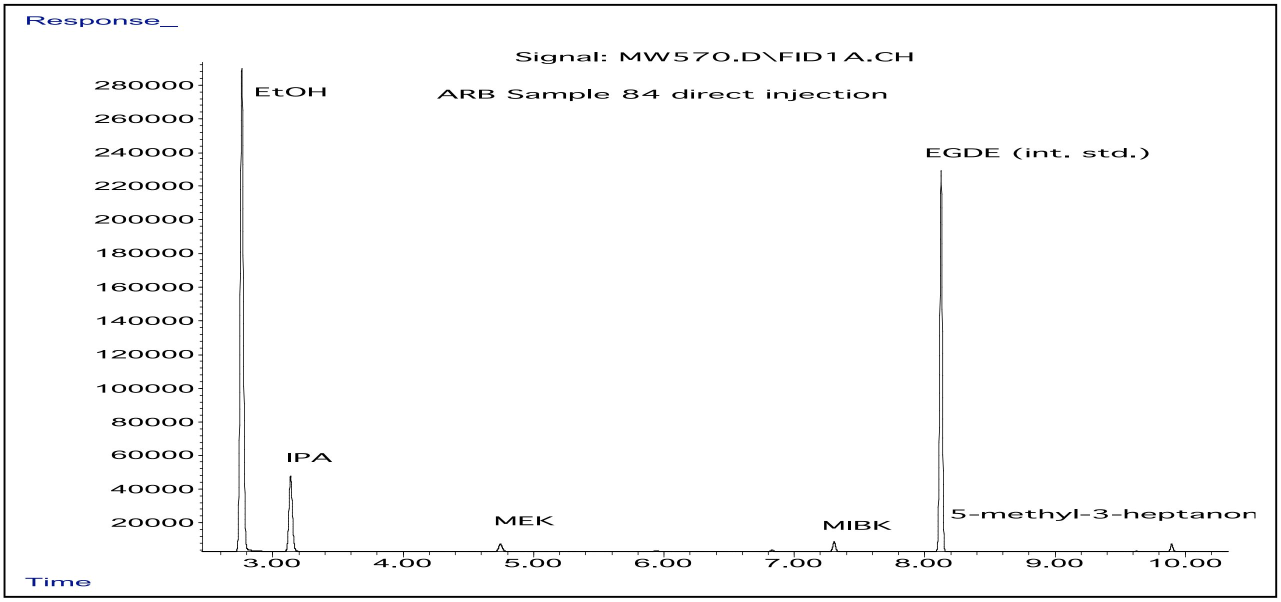
Analysis of Sample 57.2

compound	fraction
MeOH	0.0126
EtOH	0.0089
acetone + IPA	0.5771
acetone by diff	0.5434
IPA(wax)	0.0337
MeOAc	0.0016
MEK	0.0512
EGDE	0.4282
BuOAc	0.0530
EtBz	0.0145
m,p-Xy	0.0540
MAK	0.0165
o-Xy	0.0171
EB	0.0167
4-Me-3-heptanone	0.0059
total	0.2840

Direct analysis of this solventborne coating enabled the amounts of exempt compounds to be determined along with the VOC content. In addition, amounts of several hazardous air pollutants (HAPs) (methanol, ethyl benzene, xylenes) were also determined.

Sample 84: Sample 84 is a solventborne, low solids shellac. The chromatogram for this coating is shown below in Figure 3.

Figure 3 Chromatogram of Sample 84



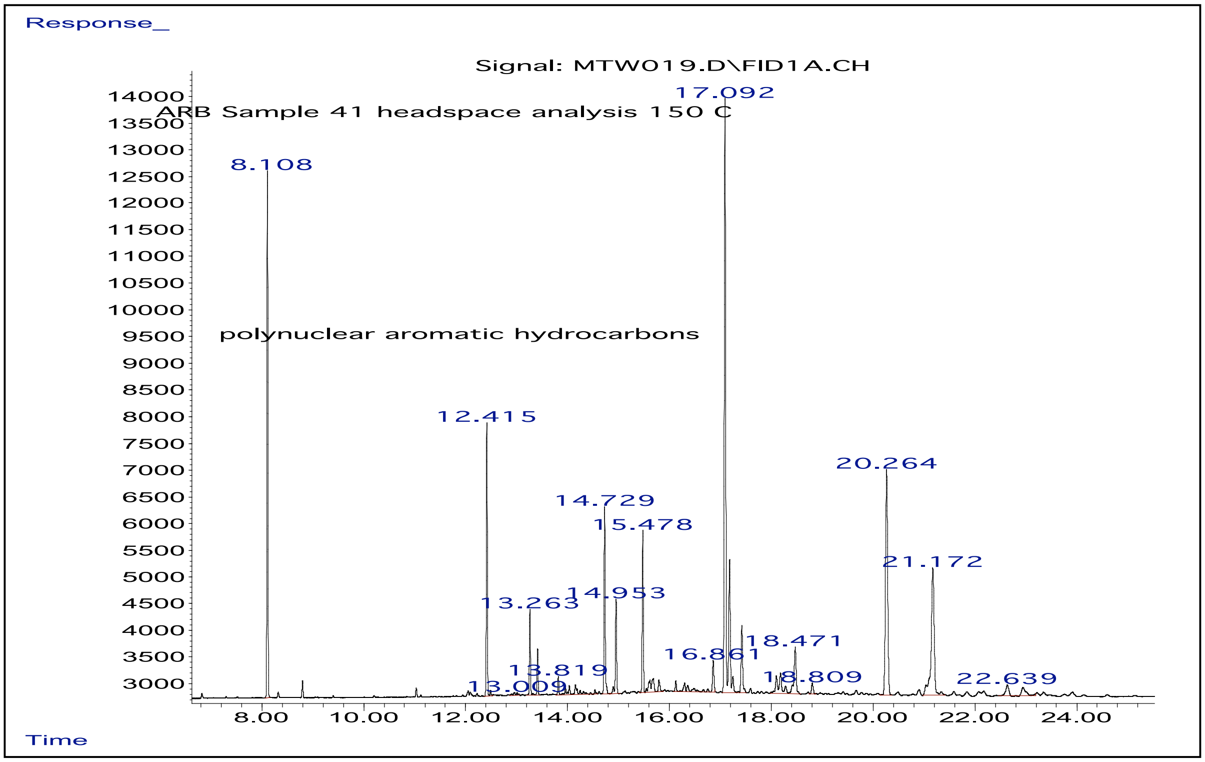
The various peaks were identified by their retention times, as usual. However, the sum of the fraction of all the volatiles and the fraction solids did not add to one. A Karl-Fisher water analysis was performed and the water content of this solventborne coating was found to be approximately 5%. The detailed analysis is shown below.

Analysis of Sample 84

cpd	fraction
EtOH	0.6032
IPA	0.0984
MEK	0.0085
2-pentanone	0.0011
ethoxyethanol	0.0015
MIBK	0.0071
EGDE (int. std.)	0.0000
5-methyl-3-heptanone	0.0049
total	0.7247
solids	0.2248
H2O by KF	0.0484
mass balance	0.9979

Sample 41: Sample 41 is a low VOC waterborne driveway sealer. Upon analysis by direct injection the chromatogram showed several peaks at retention times longer than twelve minutes which we had not encountered in any other samples. We determined these peaks were all due to polynuclear aromatic hydrocarbons. Analyzing this sample accurately would require both a direct injection and an analysis of the extracted film to determine the amount of VOCs remaining in the dried film. We decided to try analyzing this sample by headspace analysis at 110°C and 150°C. The chromatogram for the 150°C run is shown below in Figure 4. The peak at 8.1 minutes is due to internal standard.

Figure 4 Headspace Chromatogram of Sample 41



Results for fraction volatiles obtained from direct analysis (first analyzing liquid then analyzing dried film and subtracting), and headspace analysis at 110°C and 150°C are shown below.

Analysis of Sample 41

Method	fraction VOC
direct (liquid - film)	0.0215
Headspace 110C	0.0191
Headspace 150C	0.0383

The headspace results at 110°C agree well with the more complex direct analysis. Using headspace analysis may provide a method to determine VOCs of coatings with significant amounts of high boiling volatiles without having to analyze both the liquid coating and the dried film.

II. Future work

A. Validation of Test Methods

We are now ready to send samples of many of the coatings in this study to other laboratories for analysis as part of the validation study of the methods we have developed. Typically, two other laboratories will analyze each sample. We hope to have each laboratory analyze between five and ten coatings. The laboratories will be provided with one quart samples of the coatings along with whatever information we have on the coatings from the manufacturers. We will also inform the laboratories of what VOCs might be present so they can determine response factors for these VOCs. We will provide the laboratories with copies of the analysis procedures we have developed. We hope to be able to present preliminary results from these studies for our next report.

B. Completion of Analyses of Samples

During the next reporting period we will complete our analyses of all samples and begin organizing the results in their final form.

III. Overall progress of project.

Project is on time and on budget.